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PROPERTIES DESIRABLE IN PLASTIC PROPELLANTS

WITH NOTES ON METHODS OF TESTING.

BY

F. JAMES AND D.F. RUNNICLES.

REVIEW ON

May 1977

ABERPORTH, CARDS

AND

WALTHAM ABBEY, ESSEX.

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SUMMARY

This memorandum has been written for the guidance of research teams who may undertake work on plastic propellant. It enumerates what are considered the desirable properties of this kind of propellant. Methods of measurement of the rheological, chemical and ballistic properties, together with an outline of the necessary weapon clearance trials, are briefly discussed.

1. Properties desirable in a plastic propellant.

1.1. Rheological properties.

1.1.1. Propellant.

Plastic propellants are always filled against the wall of the rocket motor and this was the chief reason for their development, since this arrangement protects the motor from the propellant gases and gives a number of advantages in design. The propellant does not burn over that part of its surface which is adhering to the wall and it is essential that separation from the wall does not occur during storage. If separation occurs, the propellant will burn over the surface so produced, and the motor will develop an abnormal pressure and will burst if the separation covers an appreciable area.

The coefficients of thermal expansion of the motor body and of the propellant are of different orders but the dimensional changes resulting from changes of temperature are adjusted by plastic flow in the propellant. Under the lower stresses due to gravity, or the high but momentary stresses due to rough handling, the propellant should not flow but must retain its charge shape so that the pressure-time characteristic of the motor does not change. Under the stresses due to acceleration on firing, or due to the pressure of the propellant gases, the flow must be slow enough to give no appreciable distortion during the time of burning. Under all these stresses the propellant bulk must adhere to the motor wall without separation at any area.

These considerations give us the rheological properties of the ideal plastic propellant.

The plastic propellant should exhibit a negligible irreversible strain under stresses below a limiting value.

This limiting stress should be well above the deforming stresses due to gravity in the rocket motor.

At moderate stresses, corresponding to those developed during firing, the rate of flow should be low.

At higher stresses, corresponding to those developed by temperature changes, the flow should be adequate to avoid separation from the wall.

The cohesion, or extent of deformation without development of cracks, should be high.

The adhesion to metal surfaces should be adequate. This adhesion may be effected through a varnish layer. The use of such a layer would probably be essential in steel motors to avoid corrosion before filling.

The propellant must retain the above properties over the whole of the temperature range applicable to the weapon.

As a guide to the order of values some rheological properties are given below of a propellant which has been tried extensively in small steel rocket motors. The problem to be solved is to fit the properties between sufficient rigidity at high temperatures, and adequate flow to take up dimensional changes at low temperatures. A range in temperature from 140°F. to -5°F. has usually been taken as the Service range for rockets, and has been covered with fair success in rounds up to about 5 inches diameter. The present view, however, is that the lower limit of temperature should be extended to -40°F. or beyond, and this would demand considerable improvement in the temperature dependence of the rheological properties.

In the early development of plastic propellant the most suitable consistency, or plasticity, was determined, rather empirically, by trial in the rocket motor. At the same time simple methods of measurement were developed, so that a control could be kept on the consistency during the development of new propellants, and their subsequent manufacture on a large scale. The properties of existing plastic propellant may be defined in terms of the values obtained from these methods of measurement. The values are not absolute; although absolute values have been determined with a thixoviscometer, it is more convenient pending the development of this part of the research to use simple methods of measurement, giving comparative values.

In the routine plasticity test a 20 x 15 mm. diameter pellet of plastic propellant, shaped in a mould under a pressure of 1000 p.s.i., is subjected to a load of 850 gm., corresponding to a pressure of 7 p.s.i., applied for 30 seconds in a simple parallel plate plastometer. No provision is made to compensate for the increase in area of the pellet as it is compressed. The measurement is made at 25°C. During the 30 seconds the pellet should undergo a compression of between 20 and 40 per cent of the initial height. The cohesion is also measured in this test. After 30 seconds compression the load is maintained, or increased if necessary, until cracks first appear in the surface of the pellet. The compression should amount to at least 50 per cent before cracks first appear.

The flow of the existing plastic propellant under gravitational stresses is considerably reduced by the presence of marked strain hardening. Under small stresses this strain hardening produces a pseudo-yield value. The measurement of this yield value forms a convenient sorting test to determine whether the propellant is likely to retain its shape on storage. A 20 x 15 mm pellet of propellant, shaped in a mould at a pressure of 1000 p.s.i. is subjected to a load of 200 gm., corresponding to a pressure of approximately 1½ p.s.i. The total, or equilibrium value, of the compression should not be greater than 20 per cent of the initial height. For convenience, this test is carried out at 140°F. At this temperature the equilibrium value for the compression is reached in 15 to 20 hours. The value is little affected by temperature. It is not yet clear to what extent this strain-hardening assists in maintaining the shape of the charge during storage at high temperature, and this is one of the problems to which research is being directed.

The plastic propellant should not harden to any marked extent on storage at elevated temperatures. Most propellants have been observed to show some hardening, but it is important to distinguish between reversible or thixotropic hardening which can be eliminated by reworking the propellant between the fingers and irreversible hardening where the plasticity has been permanently destroyed. Since the satisfactory propellants show no tendency to crumble or separate from the motor wall on climatic storage (temperature cycling) it may be assumed that the stresses set up during the temperature changes are sufficient to provide a "reworking" effect and overcome the thixotropic hardening. Apart from the effect due to irreversible changes (gel formation) in the binder on hot storage the reason for the irreversible hardening is not clearly understood. It has been found during the research on plastic propellant that most of the rejections of unsatisfactory propellants are due to irreversible hardening and loss of plasticity on hot storage.

It is found that the propellants meeting these requirements, as nearly as has so far been attained, can be filled into motors by means of a press and suitable forming tools, using a load of about ½ ton per square inch. It is usual to press at an elevated temperature, say 100°F., both to obtain better adhesion and to aid the filling process.

An important field of investigation is the search for methods of inspection to ensure that charges are filled without large air-bells or surfaces of separation.

1.1.2. Binder

The binder should have a low temperature coefficient of viscosity and not be volatile at the upper temperature limit nor show any phase separation at the lower limit. None of the solid ingredients of the propellant should have any appreciable solubility in the binder. The effect of gel-formation in the binder producing hardening of the propellant has already been mentioned; degradation of the polymeric constituent of the binder, with resulting drop in viscosity, may also produce undesirable plasticity changes. The binder should preferably have good adhesion to the material, steel or light alloy, from which the motor tube is constructed. The adhesion can be improved, if necessary, by coating the rocket tube internally with a lacquer. Very few binders have been found which give propellants with all the desirable plastic properties, in particular, the absence of severe hardening on storage. An otherwise satisfactory binder with indifferent adhesion to metal should not be rejected if its adhesion can be rendered acceptable by use of a suitable lacquer.

1.1.3. Solid constituents.

Although a large number of binders have been investigated, work has been limited to only a few solid constituents. The binder has a far greater influence than the solids on the final plastic, and most of the solids investigated give satisfactory plastics. It is necessary, however, for at least one of the solids to be fairly soft so that under the rolling conditions used, sufficient fine particles may be produced without involving excessive times of rolling. Apart from the rather obvious desirabilities of the high energy content and oxygen balance, it is preferable for the solids to give gaseous and non-toxic products of combustion.

1.2. Stability.

Adequate chemical stability is essential for all types of propellant but the plastic propellant is more sensitive in this respect, since small amounts of gas will produce considerable distortion of rocket charges especially in thick webs. An end burning charge with a length/diameter ratio approaching unity will, when stored at 140°F., soon show distortion of the burning surface if there is any appreciable evolution of gas.

1.3. Ballistic Properties.

The usual desiderata for all rocket propellants, namely:-

1.3.1. The effect of pressure and of charge temperature on the rate of burning should be as small as practicable. The mechanism by which pressure and temperature influence rate of burning is as yet imperfectly known. A better knowledge in this field would show how propellants could be improved in this respect. At present, progress depends on empirical methods and it is found that plastic propellants, which contain discrete particles of some of their ingredients, have the advantage of colloidal propellants such as SU/K. A further improvement would, however, be of great practical importance.

1.3.2. "Erosion" of the propellant should be as small as practicable.

In rocket ballistics account must be taken of the effect on rate of burning of the gas velocity over the surface, a phenomenon which is termed "erosion". The mechanism of erosion is imperfectly understood and requires investigation. Plastic propellants of relatively low performance appear to be free from the effect at the gas velocities usually obtaining in the conduits of rocket motors; but it appears likely that when a high performance is sought, this advantage over colloidal propellants such as SU/K will be lost. A non-erosive propellant of high performance would have great practical advantages, especially in rockets which call for a high density of loading combined with a high length/diameter ratio.

1.3.3. High performance

It should be noted that a high performance is not required in all rockets, and that it may be useless in any rocket if obtained at the expense of other properties given in this schedule.

1.3.4. Wide range in rate of burning.

A high rate of burning e.g. several times that of SU/K at corresponding pressures, would be useful for certain limited applications.

Research should be directed to means of controlling rate of burning so that a series of propellants of widely different rates becomes available.

1.3.5. Performance, and reliability of burning, maintained at low pressures.

Colloidal propellants such as SU/K do not continue to burn reliably at pressures below about 400 p.s.i., and the performance index begins to decrease at this pressure level. The cause of this is now partly understood; the chemical reaction of the propellant gases is incomplete when they emerge from the motor. The plastic propellants so far developed burn reliably at lower pressures than 400 p.s.i., some of the plastic propellants, however, begin to lose performance at higher pressures than this.

2. Climatic and Rough Usage.

2.1. Preliminary trials.

A large proportion of the failures exhibited in plastic propellant are due to irreversible hardening and loss of plasticity on storage. The first test of a new propellant, following satisfactory results from plasticity measurements, should consist in storing a sample for 24 hours at 140°F. The sample should weigh several hundred grams and be placed in a sealed tin, to avoid any disproportionate loss of volatiles. If the sample appears to be satisfactory after 24 hours as judged by plasticity measurements, the storage should be continued for 2 weeks. These tests are a necessary preliminary to any climatic storage in rocket motors.

2.2. High Temperature Storage.

The climatic storage of rocket motors should be carried out with charges of web thickness not less than one inch. Suitable storage periods for first tests are: 1 week, 2 weeks and 4 weeks at 140°F. More extended trials carried out on full size motors consist of 2 weeks at 140°F., followed by 12 weeks at 120°F. After storage, rounds should be fired at air temperature, 140°F. and -5°F. This trial has received approval from the Service (O.B.Proc.No.U.2688).

2.3. Temperature Cycling.

A temperature cycling trial for rocket motors, which appears likely to be generally agreed upon (O.B.Proc.No.U.2755) consists of 28 daily cycles of boxed ammunition between 140°F., and 32°F., six hours or more at each temperature with two hours at air temperature at the change-over; occasional cycles should go down to a very low temperature (-40°F). For preliminary tests the number of cycles could be considerably reduced.

2.4. Rough Usage.

It has been useful to test the propellants so far developed by dropping the weapon 6 feet on to concrete at the extremes of the temperature range (140°F. to -5°F). (It should be noted that propellant SU/K barely withstood the treatment at -5°F. although no adverse reports from Service have been received of defective function due to rough handling at this temperature).

A further scheme of rough usage trials which seems likely to be acceptable to the Services is proposed in P.D.E. Note No. 19 45/10 O.B.Proc. No.U.2755).

3. Measurement of the Ballistic Properties

Satisfactory methods of determining the ballistic properties of plastic propellants have not yet been developed although some promising schemes are being tried. Methods depending on the firing of small cylinders, such as are used for colloidal propellants, are obviously not applicable. Much use has been made of 2 inch diameter charges with a cylindrical conduit expanding to a short cone at each end, the geometry of the shape being arranged to give an approximately constant burning surface. These charges weigh three quarters of a pound so that a 10 lb. batch of propellant will suffice to provide enough charges for a preliminary assessment of the ballistic properties. For more extended measurements a 3 inch diameter charge, 22 inches long, has been used. The shape is a double cone and cylinder, with both frustra, of slightly differing angle, at one end. This gives a burning surface showing less variation than the 2 inch charge. (P.D.E. report 1945/5). Conical charges however are not satisfactory in large sizes, or with hot propellants as the exposed wall becomes overheated on firing. It is important that all firings should be carried out with fully de-aerated propellant. The specific impulse determinations of these small charges should be treated with reserve until confirmation is obtained from the firing of larger charges. For most requirements, ballistic information is desired over the range 500 to 2000 p.s.i.; with slow burning propellants used in gas generating and similar devices the lower limit is extended to 100 p.s.i.

The calculation of charge design for a specific weapon cannot be carried out without knowing the law of propellant erosion, and until a satisfactory method of measuring this has been evolved, the design of charges with high density of loading is possible only by trial and error.

4. Clearance trials.

Before proposing new rocket weapons for Service it is usual to fire a series of clearance trials, which include both static and projection, at the extreme range of Service temperatures; and also to include a rough usage trial. The number of rounds fired will depend upon the kind of weapon and upon whether a range table has to be prepared from the results of dispersion trials when these are included. About 700 rounds have usually been required for trials of those rockets introduced into the Service during the war but a large proportion of those rounds were fired in order to ensure that the ammunition was reasonably safe at its upper temperature limit. With a new propellant the number could hardly be less than this. Until more experience of the behaviour of plastic propellants has been gained it is advisable to fire preliminary rounds before manufacturing the numbers required for full clearance. (This is still done with colloidal propellants although experience with these is more extensive).

5. List of Reports on Plastic Propellant. issued by Projectile Development Establishment, Armament Research Department, and Chemical Research and Development Department.

5.1. Early Reports (reports to the U.P. Propellants Sub-Committee, S.A.C.)

A.C. 943 U.P.P. 27	Monthly Interim Report.	May 1941.
A.C.1006 U.P.P. 37	" " "	June 1941.
A.C.1151 U.P.P. 50	" " "	July 1941.
A.C.1224 U.P.P. 56	" " "	August 1941.
A.C.1308 U.P.P. 67	" " "	September 1941.
A.C.1523 U.P.P. 94	Summary of Work 1941.	
A.C.1555 U.P.P.103	Monthly Interim Report	Dated 1st January 1942.

/A.C.1756

A.C.1756 U.P.P. 123 Monthly Interim Report December 1941.
 A.C.1757 U.P.P. 124 " " " January 1942.
 A.C.1901 U.P.P. 133 " " " February 1942.
 A.C.1993 U.P.P. 140 Plastic Alternative Propellants - Survey of
 lines of attack on improving physical conditions.
 A.C.2102 U.P.P. 143 Monthly Interim Report March 1942.
 A.C.2124 U.P.P. 148 " " " April 1942.
 A.C.2307 U.P.P. 164 " " " May 1942.
 A.C.2591 U.P.P. 179 " " " June 1942.
 A.C.2909 U.P.P. 189 " " " July - August 1942.
 A.C.3304 U.P.P. 213 Interim Report September - December 1942.

5.2. General Reports

Charge Shapes for U.P. Propellants A.C. 799 U.P.P. 13 (1941)
 Charge Shapes for Plastic Rocket Propellants A.C. 1550 U.P.P. 115 (1942)

Plastic Rocket Propellants A.R.D.Exp.Rep.170/43
 This report summarises the early work to May 1943)

Plastic Propellant - Statement of present state of development. A.R.D. Exp.Rep.627/44

Above report - revised to January 1945 " " " 627/44a
 Comments on A.R.D. Explosives (P.D.E.Note 1945/11
 Report No.627/44. (Proc.U.2599 (appendix)

✓ Charge Design. Double cone and cylinder shape. P.D.E. Report 1945/5

✓ Data regarding plastic propellants for rocket propulsion and other uses - A.R.D.Expl.Rep.226/45.
 This report describes the manufacturing processes and gives some ballistic properties of cordite and plastic propellant.

Note on the present state of development of plastic propellant - not issued as (March 1946)
 an A.R.D.Expl.Rep. but copies are available.

Progress report on experimental plastic propellants based on ammonium perchlorate Proc. U.2753 (Sept.1946)
 Report submitted to the Ordnance Board and published in the U Proceedings.

Propellants, plastic. Use with light alloy motor. P.D.E.Report 1946/14

5.3. Physico-chemical reports.

Plastic rocket propellant R.D.2633. A.R.D.Expl.Rep.589/44
 Density, thermal expansion and compressibility.

Thermo chemical data for Plastic Propellants R.D. 2633. A.R.D.Ballistics Rep. 26/44.
 (Revised version subsequently issued A.R.D.Ballistics Report 11/46)

The evolution of gas from plastic propellant. A.R.D.Expl.Rep.292/45.

Interim Report on the adhesion of plastic propellant to light alloy surfaces. " " " 211/46

/The

The relationship between rate of shear and shearing stress for plastic propellant R.D.2633.

A.R.D.Expl.Rep. 228/46.

Adhesion of Plastic propellant to metal surfaces (in preparation).

C.R.D.D. Rep. 203/47

5.4. P.D.E. Trials Reports.

Trial No.

Assisted launch of aircraft. Plastic Propellant Regularity series of 1000 lb. lots of R.D.2043.

52 G (1) S

Assisted launch of aircraft. Plastic Propellant. Flash and Smoke Trial with composition R.D.2043.

52 G (2)

Alternative Propellant. Functioning test of plastic composition P.295 in 2" rocket.

75 B

Alternative Propellant. Composition P.550. Effect on the dispersion of the 2" rocket.

75 D (1)

Propellants, plastic. Propellant P.633 to charge design P.D.592 (24-point star). Effect on performance and dispersion of the 5" rocket.

133 A (1)

Propellants, plastic. Propellant R.D.2633 (formerly P.633). to charge design P.D.592 (24-point star). Effect on performance and dispersion of the 5" rocket.

133 A (2)

Propellants, plastic. Propellant R.D.2633 to charge design P.D.601/1 (30-point star). Effect on performance and dispersion of the 5" rocket.

133 A (3)

Propellants, plastic. Propellant R.D.2048. Functioning of 3-inch motor to P.D.907/2.

133 C (1)

2.35-inch Spin-Stabilised Rocket. Plastic Propellant. Preliminary trial of composition R.D.2030.

140 C (1) S

5" L.A.P./R.P. Reduction of flash. Use of potassium nitrate to reduce flash of H.E.B. Plastic Propellant.

155 C (1)

Propellants, plastic. Propellant R.D.2043. Effects of high temperature storage.

133 B (1) S

Propellants, plastic. Propellant R.D.2633 to charge design P.D.882/1 and 2; performance and dispersion of the 5" L.A.P./R.P. (light alloy motor). (in preparation).

133 A (5)

5.5. Suggested schemes for Climatic and Rough Usage Trials of Rocket Ammunition.

O.B. Proc. No.U.2479 (Appendix) - P.D.E. Note No.1944/4.

Note on the storage temperatures and their duration, which ammunition should be capable of withstanding.

P.D.E. Note 1945/10. - A suggested scheme for the climatic and rough usage trials of rocket ammunition.

O.B.Proc. No.U.2755 (Meeting to discuss the above).

O.B.Proc. No.U.2688.

/5.6.

5.6. Ordnance Board Proceedings dealing with plastic propellant.

U. 2325, 2355, 2426, 2449, 2559, 2585, 2624, 2653, 2655, 2717,
2735, 2736, 2753, 2766, 2805.